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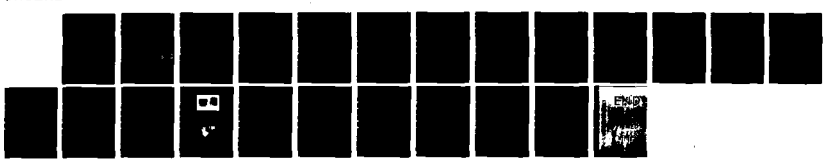

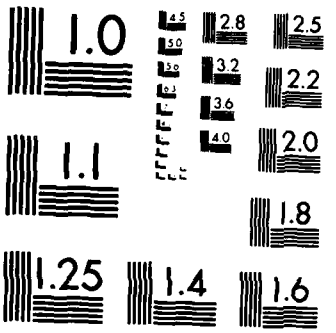

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COMPOSITE MATERIALS FOR MAXILLOFACIAL PROSTHESES

Annual Progress Report

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AUGUST 1980

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The purpose of this program is to develop ultrasoft composite materials to be used as fillers in the fabrication of maxillofacial prostheses. The projected composite systems are elastomeric-shelled, liquid-filled microcapsules. Experiments continued on the interfacial polymerization process with spherical, sealed capsules achieved. Needs identified are non-inhibition of curing of matrix materials, less diffusion of core liquid through capsule walls, and smaller capsules.

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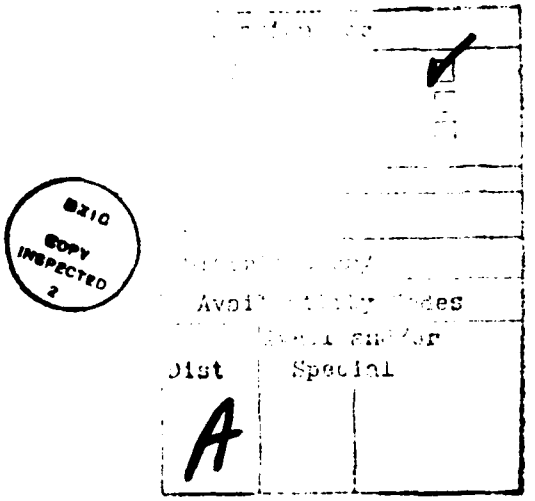
ABSTRACT

The purpose of this program is to develop ultrasoft composite materials to be used as fillers in the fabrication of maxillofacial prostheses. The projected composite systems are elastomeric-shelled, liquid-filled microcapsules. Experiments continued on the interfacial polymerization process, with spherical, sealed, capsules achieved. Needs identified are non-inhibition of curing of matrix materials, less diffusion of core liquid through capsule walls, and smaller capsules.



FOREWORD

The concept behind this program is that a multiphase composite system should be able to simulate the mechanical propertise of human soft tissue better than a homogeneous system could. The proposed composite of particular interest consists of liquid-filled, elastomeric-shelled microcapsules held together to form a deformable mass; this is to simulate the semi-liquid cellular structure of human soft tissue.

The third year's program has been devoted primarily to experimental studies on making suitable microcapsules by interfacial polymerization processes. Elastomeric-shelled capsules were obtained which were free of pinholes, with demonstrated shelf life in excess of six months. Initial studies were made of capsules in matrices, though cure inhibition of matrix material by the capsules wall material limited the useful data from these. Expanded studies with bonded structures and prototype maxillofacial parts will follow the development of improved capsules.

CONTENTS

1. INTRODUCTION

In the first annual report the history of materials for maxillofacial prostheses was reviewed. Many materials have been used, but in recent times poly(vinyl chloride) plastisols, polyurethane compositions and silicones have been used effectively in simulation of skin and external features.

An area in paticular in which further improvement is needed is in simuating the softness or "feel" of underlying soft tissues. This is particularly important if some movement capability is needed. The softest materials presently available are polymeric foams (which have the disadvantage of taking a permanent set by loss of gas when compressed) and gels (which are often unstable and lose internal liquid by syneresis).

This program is studying a new class of materials for use in fabricating maxillofacial prostheses: namely, liquid-filled, elastomeric-shelled microcapsules. Conceptually, such a product is attractive for several reasons: (2) the cells in the natural soft tissue are themselves composites of liquid (or semi-liquid) material in deformable shells; (2) the liquid-filled microcapsules could be stable entities free from the syneresis or gas-leakage of other soft materials; (3) the microcapsules could be stored as such and used by the prosthetist as an ultrasoft filler to modify other materials as needed.

Two methods for making elastomeric-shelled microcapsules were experimentally studied in the first two years of the program. One was coaxial extrusion, and the other was interfacial polymerization. In the third year of the program, efforts have been directed entirely to capsules made by interfacial polymerization methods.

2. DEVELOPMENT OF PRACTICAL TECHNIQUES FOR THE PREPARATION OF LIQUID-FILLED POLYURETHANE CAPSULES

2.1 SUMMARY

An effective and flexible process has been developed for the preparation of liquid filled polyurethane capsules of the type believed to be suitable for use in preparation of polymer composite systems.

The new method, which permits considerable latitude in the selection of urethane wall components, as well as in selection of the liquid internal phase, utilizes a two stage polymerization process in which a fragile polyurea skin is rapidly formed on a liquid droplet by interfacial polymerization as the first stage. After initial skin formation, a polyurethane wall membrane having the desired physical properties is formed by a slower, secondary process.

Capsules with strong, flexible wall membranes containing a variety of internal phases have been prepared by this method. The procedure appears to be readily adaptable to scaleup operations.

The urethane system selected for the capsule wall is of the polyether/methylenebisdicyclohexyl isocyanate type previously used to produce a low modulus, light stable, elastomeric skin. The liquid interior phase used at present for the maxillofacial prosthesis application is a non-reactive (end-capped) polypropylene glycol (Union Carbide Corp., LB-385). Many other, reactive and non-reactive interior phases can also be employed.

An important characteristic of the polyurethane wall material presently being used is its apparent ability to act as a semi-permeable membrane, with results that are both beneficial and troublesome.

The polyether internal phases currently in use appear to exude slowly through the cell wall, which produces adhesion problems when the beads are finally imbedded in their silicone rubber matrix.

It is anticipated that this problem can be controlled through use of a non-polar internal phase, application of a "seal coat" to the beads, or both.

For other applications, the semi-permeable membrane phenomenon may turn out to be highly useful by providing "slow-release" of a desired internal phase to the environment, as for example in the design of drug delivery systems or a catalyzed chemical reaction process.

In this report the new capsule forming system is described in detail, along with some of the modifications which have been considered to date.

2.2 TWO-STAGE DROP INTERFACIAL POLYMERIZATION SYSTEM (PLS 122-19)

2.2.1 External (Continuous) Phase

Kerosene (Fisher, deodorized, 97 wt. %), 1-7 diamino heptane (Aldrich D1740-8, 1 wt %), and fumed silica (Cabot Corp., Cab-O-Sil or PPG Corp. Hi Sil T 600, 2 wt %) are mixed with a high speed mixer to form a thickened exterior phase. The silica thickener is required to control the rate of fall of the liquid droplets through the exterior phase during the 1st stage of cure. The silica level is dependent on viscosity of the droplet phase. 1,'7-Diaminoheptane reacts rapidly with the droplet to form a fragile "skin" which protects the capsule during the polyurethane formation.

2.2.2 Interior (Droplet) Phase -- Preparation of Reagents

The interior phase consisted of:

(B-1) a mixture of linear and chain-branched isocyanate terminated prepolymers
(B-2) a mixture of linear and chain-branched polyols capable of reacting with (B-1) to form a polyurethane
(B-3) a 3' amine catalyst (triethylenediamine)
(B-4) an inert polar liquid
(B-5) a trace of non-reactive dye (eosin) to facilitate identification of the beads.

B-1 - Isocyanate-Terminated Prepolymers

A linear isocyanate-terminated prepolymer was prepared from the polyol (Pluracol 2010, BASF Wyandotte Corp, 200 g), methylenebisdicyclohexyl

isocyanate (Hylene W, DuPont, 62.4 g) and 1,'4-diaminobicyclooctane (DABCO, Air Products Co., 1.0 g) by mixing the reactants, under dry nitrogen and warming to 50°C for 4 hours. A chain-branched, isocyanate-terminated prepolymer was prepared from a mixture of:

Pluracol P-2010 (Wyandotte)	200.0 g
Pluracol PeP450 (Wyandotte)	26.0 g
Hylene W (DuPont)	190.0 g
DABCO (Air Products Company)	2.3 g

by mixing the reactants and warming them to 50°C for 4 hours.

The linear and branched chain prepolymers were mixed in the ratio 90 linear/10 branched (w/w) for use in capsule formation.

B-2 - Polyol Mixture

P-2010 (97 parts) and PeP450 (3 parts) were mixed to form a reactive polyol phase capable of reaction with the isocyanate terminated prepolymers (B-1) to form a polyurethane. At ambient temperatures, the reaction time between B-1 and B-2 was 4-12 hours, even in the presence of catalyst (B-3), which allowed ample time for mixing and bead formation before the curing reaction occurred.

Reagent B-4, inert polyol (LB,385, Union Carbide Corp.) and B-5 (Eosin) were added as shown in the following formulation schedule.

2.2.3 Interior (Droplet) Phase Formulation

The basic interior phase formulation used for capsule formation was:

Linear Prepolymer (PLS-122-17-1)	39.6 g
Branched Prepolymer (PLS-122-17-2)	4.4 g
Pluracol P-2010 (97%) 11.52 g	11.52 g
Pluracol PeP-450 (3%) 0.36g	0.36 g
DABCO 0.12 g	0.12 g
Inert Polyol (LB-385)	44. g
Eosin (for color)	trace

The mixture was stable for 1-4 hours.

2.2.4 Preparation of Polyurethane Capsules by Drop-Interfacial Polymerization

The freshly mixed external phase (A) was placed in an open vessel containing a suitably sized polypropylene mesh basket for collection and isolation of the capsules.

The freshly prepared internal phase was charged to a motor-driven syringe fitted with a suitable needle (long, curved 22 gauge needle was found to be suitable for many preparations, but other sizes of needle can be used).

The internal phase was added dropwise to the curing bath with the needle tip approximately 2-4 cm above the bath surface. A variable speed turntable was used to rotate the curing bath to provide a fresh surface for each droplet.

The droplets immediately formed a fragile (polyurea) skin. They were allowed to remain in the curing bath for 1 hour and were then removed from the bath (via the mesh basket), rinsed with a dilute nonionic detergent solution (1% Titron X-100, Rohm and Haas Company), dried and stored in a closed jar.

As initially prepared the capsules were fragile because of the low-strength, polyurea skin. However upon standing overnight the polyols present in the internal phase continued to react in the presence of catalyst to form a strong and tough, flexible, elastomeric capsule capable of extensive deformation without rupture.

2.3 DISCUSSION OF PRINCIPAL VARIABLES

The drop-interfacial technique for polyurethane capsule formation described herein is capable of wide variation for the control of physical properties as well as variation in the material encapsulated. The principal variables in the process are discussed below, along with various positive and negative features of the process.

2.3.1 Physical Properties

The interior (droplet) phase is a complex system capable of modification for control of properties. For example --

The isocyanate terminated prepolymer ratio can be altered infinitely to control the crosslink density, the urethane group spacing, and, as a result, the modulus, tensile properties, porosity, and elasticity of the urethane membrane. Effectively any practical polyurethane system can adapted for use in the process through control of the polyurethane react ı rate.

2.3.2 Isocyanate Type

Non-discoloring (aliphatic) isocyanates are used in this process to provide color stability. These isocyanates react relatively slowly with polyols at ambient temperature even in the presence of catalysts.

Where desired, (lower cost) aromatic isocyanates can readily be used in the process. These react more rapidly than aliphatic isocyanates but the required work life of the internal phase can be maintained by reducing or eliminating the catalyst.

Polyester or polyamide type, isocyanate-terminated prepolymers can be substituted for polyether based prepolymers in the present process. For maxillofacial prosthesis applications, these types of prepolymers were considered less desirable than polyether types because of the generally higher moduli they impart and also because of the possibility of hydrolytic instability.

Urethane catalysis. Most low temperature polyurethane processes require the use of a catalyst. In the present process either an amine catalyst (1,4 diaminobicyclooctane, "DABCO") or a tin compound (stannous octoate) were found to be effective. Other urethane catalysts and even heat (reaction at 50-80°C) could be used in place of the present catalysts if desired.

2.4 ENCAPSULATED MATERIAL

In theory any material inert to isocyanate and/or hydroxyl reaction can be encapsulated. In addition to the non-reactive polyether (LB-385) presently

used, any other liquid or solid material can be employed. A list of some of the interior phases tested to date is given below.

Low MW (Union Carbide LB 65)	exudes rapidly
Intermediate MW (Union Carbide LB 385)	exudes slowly
High MW (Union Carbide 50 HB-1000)	slowest

Other encapsulated materials are listed in Table 1.

Because the polyurethane skin functions as a semi-permeable membrane, the molecular weight of the encapsulated phase is important. Low molecular weight materials exude more rapidly than high molecular weight materials, as has been demonstrated with a series of inert polyols.

TABLE 1

LIST OF MATERIALS ENCAPSULATED IN THIS STUDY

Amyl acetate	(PLS 122-29)ff)
Nitrobenzene	(PLS 122-36-1)
Acetophenone	(PLS 123-36-2)
Ethylene dibromide	(PLS 122-37-1)
Iodine	(PLS 122-37-2)
$CuCl_2$ (solid)	(PLS 122-38-1)
Ni Cl_2 (solid)	(PLS 122-41)
Potassium chromate (solid)	(PLS 122-38-2)
Potassium ferricyamide (solid)	(PLS 122-42-1)
B-limorene	(PLS 122-39)
Naphthalene (solid)	(PLS 122-40)
Pine oil	(PLS 122-42-2)

It is probable that the rate of release of the interior phase from the capsules can also be controlled by increasing the crosslink density of the skin, as well as by controlling the polarity of prepolymer materials used to construct the skin. For polar encapsulates, a less polar skin and for non-polar encapsulates a more polar skin can be used.

The major requirement for selection of the internal phase is that it should not react with the isocyanate group present in the internal phase prior to and during the urethane reaction.

Admittedly this is a serious limitation because it prohibits the use of many reactive materials (i.e. alcohols, amines, free carboxylic acids, etc.). Nevertheless it is equally obvious many important types of materials can still be encapsulated by the method, and it appears that even reactive materials may be incorporated by an infusion process (on which further investigation is needed).

On the positive side, the process provides a way to make relatively strong, stable, capsules in situ in a new and useful way.

3. STUDIES OF MECHANICAL PROPERTIES OF CAPSULES AND BEHAVIOR IN A MATRIX

3.1 STABILITY OF CAPSULES

Of all the capsules made to date, none were found to be completely acceptable based on the combined standards of not bleeding out (exuding) of the core material and of not becoming too hard. Capsules having the desired elasticity and softness tend to bleed, and those that do not bleed have high-modulus skins or cure completely through to a solid bead. The depth of solidification appears to be related to the isocyanate-terminated prepolymer content. The capsules containing about 22% prepolymer are soft and liquid filled, while those containing 44% prepolymer become solid thoughout in several days.

The most stable batch (122-25) used for this work had thin soft shells that remained acceptably thin on standing for several months and continue to remain stable, although they slowly bleed core material onto their outer surfaces.

3.2 COMPATIBILITY WITH CASTABLE ELASTOMERS

The compatibility of the microcapsules in castable elastomers is poor with regard to cure inhibition. Generally, the degree of inhibition toward curing of matrix material to the elastomeric state is proportional to the density of the mirocapsule population. That is, a few capsules in an elastomer precursor only cause inhibition at the capsule/elastomer interface while a high density of capsules causes inhibition throughout the elastomer matrix. Figure 1 shows two cubes of Dow Corning silicone elastomer MDX-4-4210 containing microcapsules. This is how the cubes appeared upon removal from their molds. The entire center sections of these cubes were not cured. Figure 2 shows the results obtained when microcapsules are added to Indpol Monothane A-10 urethane. The completely cured control cube (with no capsules) had only half as much curing cycle as the inhibited capsule-containing sample.

Figure 1. Cast cubes of polyurethane-shelled capsules in a matrix of MDX-4-4210 silicone elastomer, showing inhibition of cure.

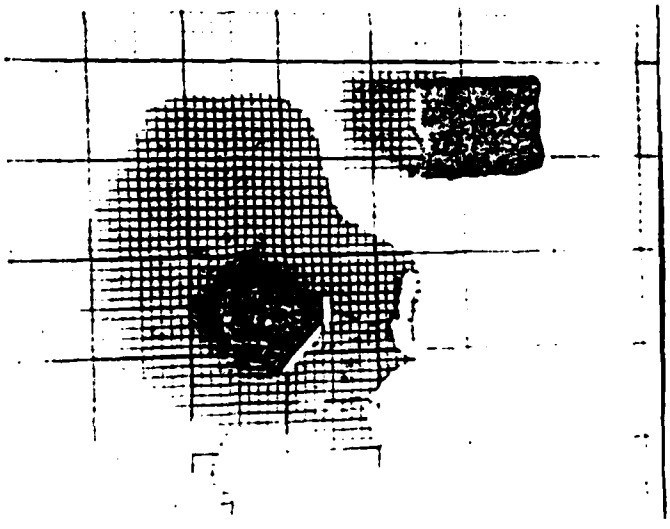


Figure 2. Cubes cast with Monothane A-10 urethane: lower left, cure inhibition caused by incorporation of polyurethane-shelled capsules; upper right, control sample (no capsules).

Attempts were made at forming cubes using GE silicone RTV 106 adhesive/sealant (red, air curing), Dow Corning 382 Medical Grade Elastomer and Dow Corning RTV 3145 adhesive/sealant (non-corrosive, air curing). Of these three materials, the RTV 3145 was least inhibited, and when prepared with a low density of capsules, showed some adhesion to the capsule walls. The desired capsule density could not be obtained with any of these elastomers.

Washing the microcapsules for several minutes in a zinc sulfate solution just before use reduced the inhibition -- which apparently is due to the presence of amines -- but did not eliminate it. Only short washes in the zinc sulfate were allowed since the immersed capsules absorb water. If excess water is absorbed, the entire content of the capsule core is bled out quickly.

Since no method had been found for preventing inhibition (and this includes altering the composition of the capsule) satisfactory test cubes could not be made. However, by first preparing a thin elastomer shell over five sides of a cube mold, and then adding the capsules and a top layer, a cube containing capsules was formed and tested.

3.3 MECHANICAL PROPERTIES OF SINGLE CAPSULES AND COMPOSITES

Silicone Elastomer MDX-4-4210 was chosen as the encapsulating material for the microcapsules. It has a lower modulus than the other silicones tested, is easy to handle, and has reasonably high tear strength

A test rig was devised, using a micrometer for loading and measuring the deflection and two strain gages mounted on a deflection beam for measuring the applied load. The output from the stain gages was plotted on a strip chart recorder calibrated to 400 grams load, full scale. The load was applied by a flat faced rod having an area of 0.32 cm^2. The loading bead was smaller than the cubes. This reduced the problem of the effect given by the stiff corners of the filled cube.

Single beads were smaller than the loading head, thus the contact area under load changed as the load was increased.

Figure 3 shows the results for compressing solid MDX-4-4210, a shell of MDX-4-4210 over the capsules and a solid cube of Monothane A-10 urethane. Since the very soft Monothane urethane has a durometer hardness of A-10, the similarity to the liquid-filled capsule sample suggests that its hardness is also about A-10. This similarly is also true for a solid Monothane bead (same size as the capsules) in comparison to a microcapsule as shown in Figure 4.

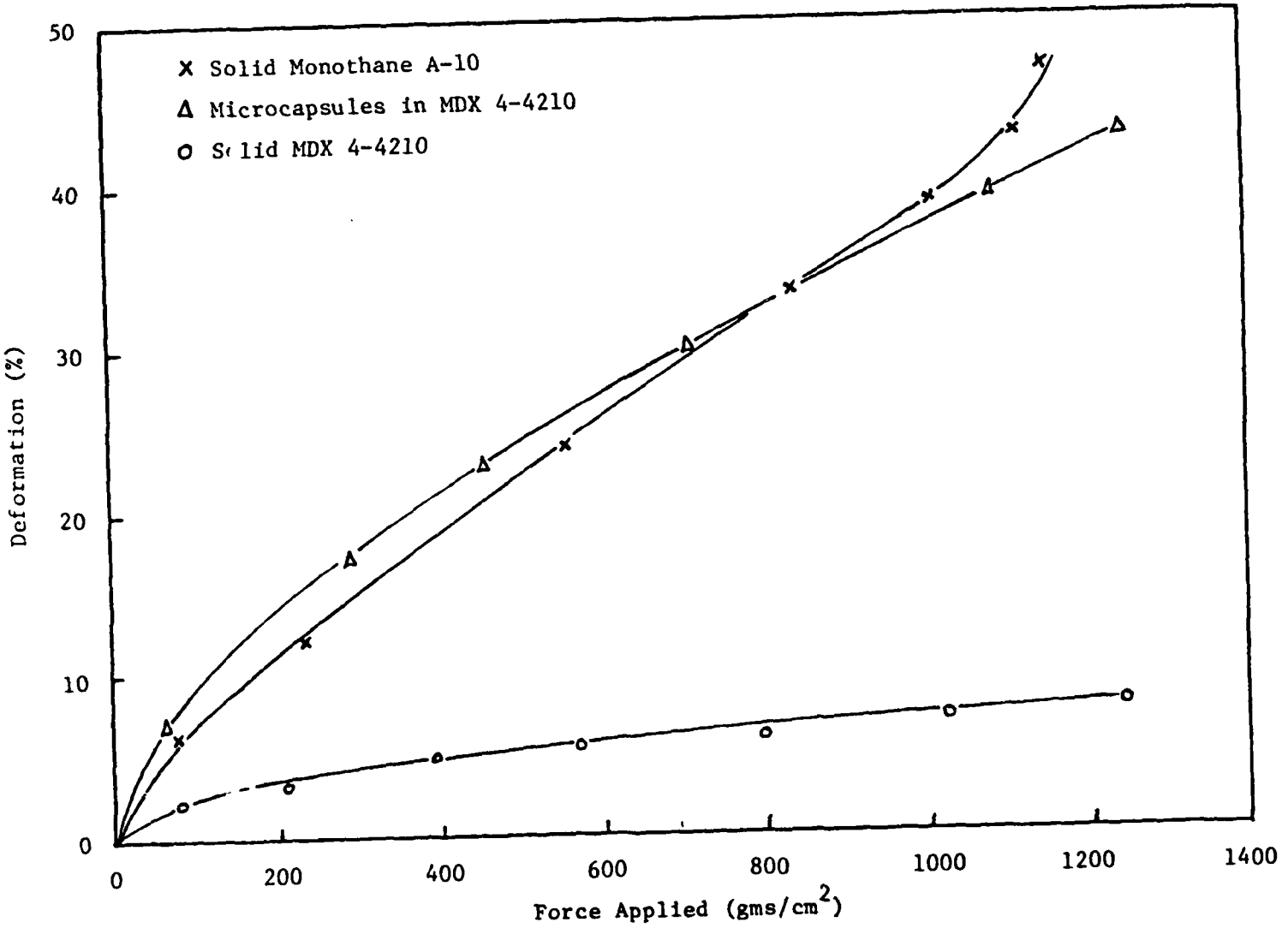


Figure 3. Compression Loading of Elastomeric Cubes

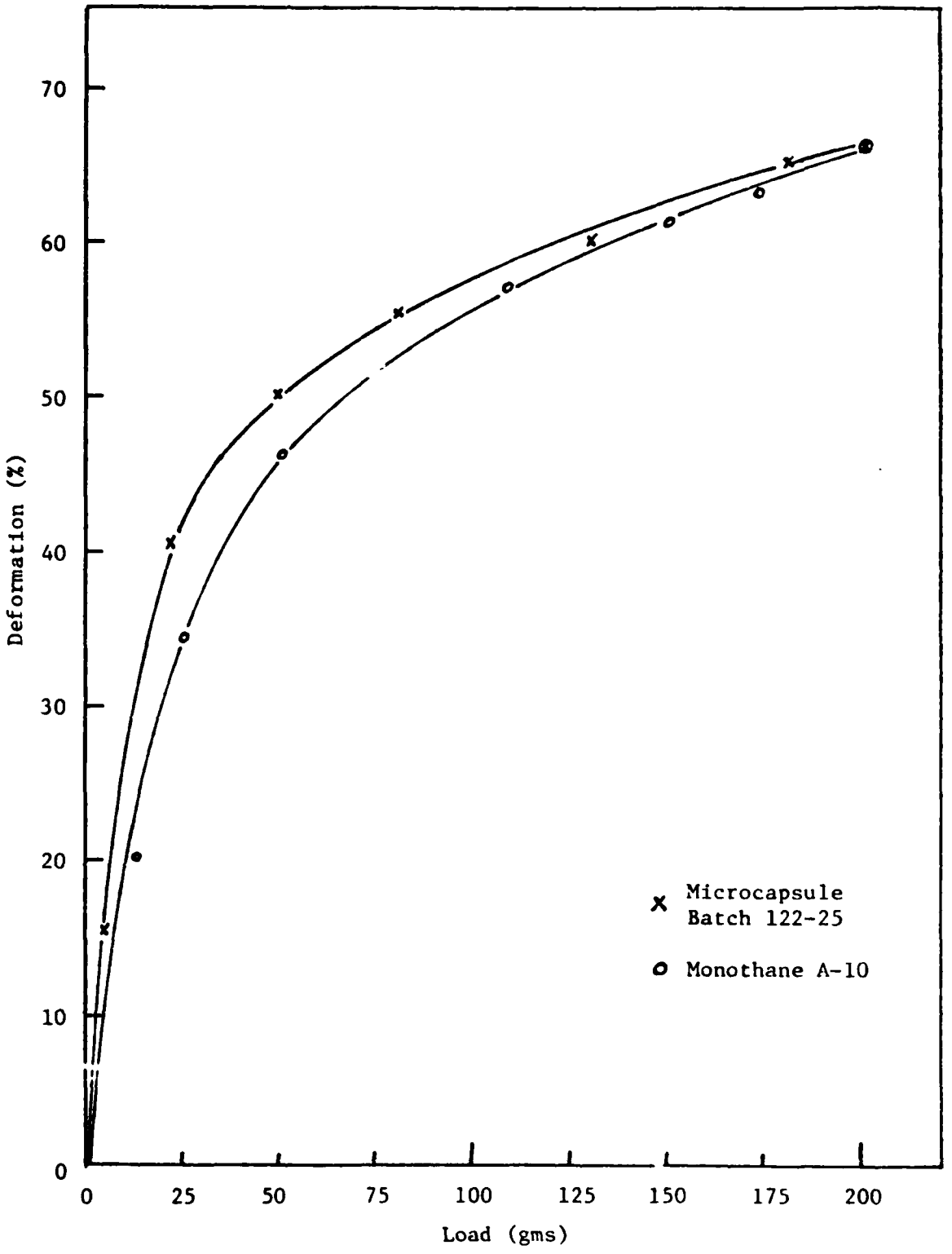


Figure 4. Compression Loading of Single Elastomeric Beads

4. FUTURE PLANS

The liquid-filled elastomeric-shelled capsules in their present state of development already represent a product with some of the requisite properties for practical application: a tough shell combined with reasonable softness of the composite capsule, a spherical shape, and a system free of pinholes.

We plan to address three residual problems, which are listed as follows with projected approaches for their solution:

1. Cure inhibition. This is not only an obstacle to practical applications in elastomeric matrices, but also impedes the laboratory evaluation of the mechanical properties of systems containing the capsules. Our first approach will be to reformulate the urethane system with organotin catalysts in place of the amine catalysts. (Amines of the type used to prepare the capsules are known to inhibit organotin catalysts -- such as are used with Silastic 382 and MDX-4-4210 -- by complexing them.) Dimethyl tin derivatives are contemplated for catalyzing the urethane reaction because they would provide faster urethane cures than the stannous octoate studied earlier. If a suitable capsule-forming approach with tin catalysts cannot be obtained, we then plan to renew the investigation of methods for reacting with or removing residual inhibitors.

2. Exudation/diffusion of core liquid. This tendency appears to be related to the type and molecular weight of the inert liquid. We plan to study a variety of inert liquids to determine the effect of structure and molecular weight on diffusion from the capsules, as well as on physical properties.

3. Excessive size of capsules. To be used as a practical filler system, the diameter of the capsules should be substantially less than the thickness of the prosthetic structure to be fabricated. The present capsules, at about 2 to 3mm diameter, are too large for most applications. Efforts will be made to prepare capsules in diameters of 0.5mm and less. Approaches which will be considered are: using smaller diameter needles (than the present 22 gauge) for droplet formation, and employing vibration techniques to produce smaller droplets.

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